NASA Technical Memorandum 103265

Graphite Fluoride Fibers and Their Applications in the Space Industry

Ching-chen Hung
Lewis Research Center
Cleveland, Ohio

Martin Long and Therese Dever
Cleveland State University
Cleveland, Ohio 44115

Prepared for the
1990 AIChE Summer National Meeting
San Diego, California, August 19–22, 1990

NASA

GRAPHITE FLUORIDE FIBERS AND THEIR APPLICATIONS IN THE SPACE INDUSTRY

Ching-cheh Hung
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

Martin Long and Therese Dever
Cleveland State University
Cleveland, Ohio 44115

SUMMARY

Characterization and potential space applications of graphite fluoride fibers from commercially available graphitized carbon fibers are presented in this report. Graphite fluoride fibers with fluorine-to-carbon ratios of 0.65 and 0.68 were found to have electrical resistivity values of 10^4 and 10^{11} Ω-cm, respectively, and thermal conductivity values of 24 W/m-K and 5 W/m-K, respectively. At this fluorine content range, the fibers have tensile strength of 0.25±0.10 GPa (36±14 ksi), Young's modulus of 170±30 GPa (25±5 Msi). The CTE value of a sample with fluorine-to-carbon atom ratio of 0.61 was found to be 7 ppm/°C. These properties change and approach the graphite value as the fluorine content approaches zero. Electrically insulative graphite fluoride fiber is at least five times more thermally conductive than fiberglass. Therefore, it can be used as a heat sinking printed circuit board material for low temperature, long life power electronics in spacecraft. Also, partially fluorinated fibers with tailor-made physical properties to meet the requirements of certain engineering design can be produced. For example, a partially fluorinated fiber could have a predetermined CTE value in -1.5 to 7 ppm/°C range and would be suitable for use in solar concentrators in solar dynamic power systems. It could also have a predetermined electrical resistivity value suitable for use as a low observable material. Experimental data indicate that slightly fluorinated graphite fibers are more durable in the atomic oxygen environment than pristine graphite. Therefore, fluorination of graphite used in the construction of spacecraft that would be exposed to the low Earth orbit atomic oxygen may protect defect sites in atomic oxygen protective coatings and therefore decrease the rate of degradation of graphite.

INTRODUCTION

Graphite fluoride is a product of graphite fluorination. The graphite to be fluorinated can be either intercalated graphite (i.e., chemically modified graphite with certain chemicals inserted between the graphite planes) or pristine graphite. Compared to pristine graphite fluorination, intercalated graphite can be fluorinated at lower temperature, which results in less structurally damaged graphite fluoride products. Direct fluorination of pristine graphite crystals by fluorine gas at 400 to 650 °C has been studied in laboratories worldwide for more than 50 years (ref. 1). Fluorination of intercalated graphite by fluorine gas at a temperature higher than 200 °C was also studied in the past 15 years (ref. 2). The graphite fluoride powders thus produced has been used as a lubricant and the cathode material in lithium battery (ref. 3).

Recently, the graphite fluorination process was modified at NASA Lewis Research Center in order to produce graphite fluoride in fiber form for more extensive applications (refs. 4 and 5). The graphite fluoride fibers thus obtained were then characterized. In this report, previous fluorination process and characterization results are reviewed briefly. Further characterization of graphite fluoride fibers to determine its durability in LEO A/O (lower Earth orbit atomic oxygen) is also presented. Potential space applications for the graphite fluoride fibers are then explored.

PREVIOUS RESULTS

Fluorination Process

Commercially available pitch based graphitized carbon fibers having modulus of 376 to 890 GPa (55 to 130 Msi) and interplanar spacing of 3.37 to 3.42 Å were used as the reactants for fluorination. These fibers were at first intercalated with a number of different halogens, including bromine, fluorine, iodine, and iodine chloride, at -7 to 150 °C, and then went through several cycles of fluorination and defluorination at 300 to 400 °C. This process resulted in graphite fluoride fibers with fluorine to carbon atom ratio in 0 to 0.68 range. The type of fibers and the intercalants used in the intercalation process, the degree of completeness and the temperature of the intercalation reactions, and the fluorination and defluorination temperature and time, all affect the physical properties of the graphite fluoride fiber products (refs. 4 and 5). Therefore, the graphite fluoride fabrication process needs to be optimized in order to have the most desired physical properties for any particular application.

Physical Properties

Graphite fluoride fibers with fluorine to carbon atom ratios of 0.65 and 0.68 were found to have electrical resistivity values of 10^4 and 10^{11} Ω-cm, respectively, and thermal conductivity values of 24 and 5 W/m-K, respectively. The coefficient of thermal expansion (CTE) value of a sample with fluorine to carbon atom ratio of 0.61 was found to be 7 ppm/°C. Using the bending method described by Sinclair (ref. 6), the tensile strength and Young's modulus of the fibers with fluorine to carbon atom ratio in the 0.65 to 0.68 range were estimated to be in the ranges of 0.48 to 1.0 GPa (70 to 150 ksi) and 140 to 200 GPa (20 to 30 Msi), respectively. This method is known to give an accurate Young's modulus value, but to give the tensile strength three times the true value. Therefore, the true tensile strength of this fiber is believed to be in the 23 to 50 ksi range. For fluorinated graphitized carbon fibers with fluorine to carbon atom ratio less than 0.65, the above-described properties change, and approach the graphite value as the fluorine content approach zero. The physical properties as functions of the fluorine to carbon ratio for the typical graphite fluoride fibers are described in details elsewhere (refs. 4 and 5).

The contact angles between individual graphite fluoride fibers and epoxy (cured and uncured) were found to be near zero. Therefore, the graphite fluoride fiber is believed to be compatible with epoxy, and a graphite fiber-epoxy composite with reasonable mechanical strength can be fabricated (ref. 5).

Composites made from 50 wt % of different kind of commercially available graphite fluoride and 50 wt % of PTFE were made by Custom Compounding Inc., and were found to have reasonable mechanical strength for manual handling (ref. 7). This demonstrates the compatibility between graphite fluoride and PTFE.

LOW EARTH ORBIT ATOMIC OXYGEN DURABILITY SIMULATION TEST

Since the chemically active atomic oxygen is present in lower earth orbit in space, durability of a material at atomic oxygen environment needs to be known before it is exposed to the LEO environment. In the present work, the fibers were tested in a simulated low Earth orbital atomic oxygen (A/O) environment, which was a 100 W, 13.56 MHz asher, operated at 70 μm pressure of air, and produced 0.1 eV atomic oxygen at a Kapton equivalent flux of 2×10^{15} atoms/(cm^2-sec) (ref. 8).

Ten different samples were studied in this test. These included three different pitch based graphitized carbon fibers from Amoco Corporation (P-25, P-55, and P-100), P-25 containing 0.6 percent fluorine, P-55 which had been in direct contact with 350 °C fluorine but gained no weight during this process, P-100 containing 3.7 percent fluorine, P-100 containing bromine 18 percent of carbon weight, P-100 containing bromine and fluorine 14 and 12 percent of carbon weight, respectively, P-100 containing fluorine 97 percent of carbon weight and trace of bromine, and an S fiberglass sample.

One strand of every of the 10 sample described above were placed in a glass vail whose cover was removed. The glass vail containing the samples were then placed in the simulated A/O environment for 20 hr. From the atomic oxygen flux value given above, the kapton equivalent fluence for this experiment was calculated to be 1.44×10^{20} atoms/cm^2. Actual fluence received by the fiber samples was much lower than the calculated value because the glass container and the 2000 fiber filaments which formed one sample strand protect each other. The weight of every sample was measured before and after the simulated A/O environment exposure.

Sixteen fiber filaments, two from every fiber sample described above except the two samples containing 18 and 14 percent bromine, were placed on three microscope slides. Both ends of every filament were held on the glass slides by silver paint. The three slides were then placed in the simulated A/O for 20 hr. During this 20 hr the samples were taken out five times to examine the changes after 10 min, 20 min, 30 min, 1 hr, 5 hr of simulated A/O exposure. Using an ohmmeter and an optical microscope (x780), the electrical resistance and the diameter, respectively, were measured before and after the above described simulated A/O exposure time. The filaments were then removed from the glass slides to the SEM sample holders. Scanning electron microscope is then used to examine the structural damages and to determine the oxygen content of the exposed fibers.

Table I summarize the weight, electrical resistance, and the diameter result of this experiment. It shows that fibers containing a small amount of fluorine have less percent weight loss and resistance changes than their pristine counterparts do. This suggested that, after adding small amount of

fluorine to the graphite fibers, the fibers become more inert to the A/O environment. It also suggests that more graphitized fibers (interplanar spacing closer to 3.35 Å) are more stable in A/O environment, that adding only bromine to the fibers reduces their A/O environment stability, and that fiberglass (SiO_2, a material known to be inert in atomic oxygen because its silicon molecules has already fully bounded to oxygen), has less weight loss than any other sample in this experiment.

The diameter data obtained from the x780 optical microscope are more complicated than the weight and electrical resistance data. Fibers may become bigger or smaller after the simulated A/O environment exposure. However, it is clear that every fiber except fiberglass became nonuniform in diameter along their length after the simulated A/O exposure, and that some fibers disappeared completely, presumably eroded by atomic oxygen.

The observation of increasing fiber diameter after simulated atomic oxygen exposure is because some fibers deformed or cracked near the fiber surface. This can be observed by scanning electron microscope, but cannot be observed by the x780 optical microscope, which observe only the shadow of the fiber.

Figure 1 shows the microphotograph of a single P-55 fiber which was exposed to the simulated LEO environment. In this photograph, several points along the length of the fiber were more damaged than the rest of the fibers. This type of structural damage was extensive if the fibers had not been fluorinated before the simulated A/O exposure, but were found only occasionally if the fibers were fluorinated beforehand.

Based on the above-described observations, it is suggested that atomic oxygen attacks the defect sites on the fibers, causing structural damage, generating more defect sites for further atomic oxygen attack, creating the most damaged area shown in figure 1, and eventually spread the damages throughout the entire fibers. More graphitized carbon fibers have less defect sites, and therefore are more durable in atomic oxygen environment. Also, adding small amount of fluorine to the fibers may leave fluorine bound to the defect sites, therefore protecting the defect sites from atomic oxygen attack, and improving the fiber's durability in atomic oxygen environment.

On the other hand, adding bromine into the fibers results in intercalation, during which bromine works its way into the fiber and eventually stay between the graphite plane. This process creates some defect sites, but cannot help protecting the defect sites from atomic oxygen attack. As a result, adding bromine to the fiber decreases the fiber's durability in atomic oxygen environment.

Figures 2 and 3 are EDS data for, respectively, a pristine P-100 filament and a P-100 filament containing 3.7 percent fluorine after they were exposed to the simulated A/O environment for 20 hr. The peak for the 3.7 percent fluorine is barely visible in figure 3, indicating that small amount of light element may not be detected by the SEM used in this experiment. The aluminum peaks came from the SEM's sample holder. The scanning electron microscope was operated at 10 kV. This voltage is so low that, based on the Monte Carlo method stored in SEM's computer, only the region within less than 1 μm from the surface of the fiber was analyzed. By comparing the ratio of the oxygen to carbon peak heights in these two figures, it is suggested that the oxygen

content near the fluorinated fiber surface is lower than that near the surface of the fiber which was not fluorinated.

Figures 2 and 3 also show that silicon and sodium are present on and near the surface of the fibers exposed to the simulated A/O environment. They are believed to come into the fiber during the simulated A/O exposure, due to silicone contamination from vacuum grease.

The results described in figures 1 to 3 were obtained from the individual single filaments after they were placed on glass slides and exposed to the simulated atomic oxygen. The most damaged spots and the contamination observed in these figures are much worse than those observed from the fiber strand samples exposed to the simulated atomic oxygen while they were in the open glass vials. However, the contamination described in figures 2 and 3 suggests the need to determine if such contamination could affect the results and conclusions in this report. Therefore, one more A/O exposure run was conducted. Four fiber strands were placed on quartz slides and exposed to a contamination-free simulated atomic oxygen environment (ref. 9). The Kapton equivalent fluence in this run was 3.32×10^{20} atom/cm^2. The four samples were pristine P-100, P-100 containing 3.7 percent fluorine, pristine P-55, and P-55 containing trace fluorine. The percent weight loss of these four samples were 30.4, 24.6, 35.9 and 70.1 percent, respectively. From these weight loss data, using the method described in the next paragraph, the erosion yield was estimated to be 2.5×10^{-25}, 2.0×10^{-25}, 3.0×10^{-25}, and 6.9×10^{-25} cm^3/atom, respectively. This result also showed that more graphitized carbon fibers are more atomic oxygen resistant then the less graphitized fibers, and that 3.7 percent of fluorine in carbon fibers appears to slightly increase their inertness in atomic oxygen environment. The one exception is that trace amount of fluorine (300 mg fibers showed $\lesssim$0.1 mg weight change during fluorination) in the fiber hurt the fiber's inertness in clean A/O environment.

Erosion yield of these fibers can be estimated as follows: Assuming that the fibers are totally exposed to the atomic oxygen flux, and the fractional mass remained after exposure is equal to the fractional volume remained after exposure, then the ratio of the average diameter of the cylindrical fibers after the simulated A/O environment exposure to that before the exposure can be calculated. Using this calculated ratio, and knowing the diameter change caused by the exposure is equal to twice the value of the surface recession, the erosion yield of the fibers can then be calculated from the following equation:

$$Y = [1-(m/m_o)^{0.5}]d/(2F)$$

where Y is erosion yield in cm^3/atom, m and m_o are the masses of the fibers after and before the exposure, respectively, d is the fiber diameter, and F is the fluence in atom/cm^2. However, the erosion yield calculated from the above equation may be lower than the true erosion yield value because the quartz slide blocked 50 percent of the fluence, and the 2000 fibers which formed one single strand of the tested sample protected each other.

POTENTIAL SPACE APPLICATIONS OF GRAPHITE FLUORIDE FIBERS

Graphite fluoride carries a rare combination of physical properties. As a result, it may be used to solve some design problems in space applications in particular, and in industrial applications in general. The following paragraphs in this section of the report list some physical properties of these materials and how they may be useful in some space applications. However, more detailed quantitative analysis is needed before actually using this fiber for the applications described below.

Improved LEO A/O Durability

The above data on A/O durability concluded that fluorinated graphite fibers containing fluorine 3.7 percent of carbon weight are more durable in the LEO A/O environment than pristine graphite. Also, the higher the degree of graphitization, the more durable the material is. Therefore, if the carbon-carbon composite that will be used in the construction of a spacecraft radiator that would be exposed to the LEO A/O is made from more graphitized carbon (e.g., pyrolytic graphite and P-75 or P-100 fibers made by Amoco), then the LEO atomic oxygen durability could be increased. Further improvement in atomic oxygen resistance could be achieved if the carbon-carbon composite described above was fluorinated so that the surface of the composite contains a small amount of fluorine. The optimum fluorine content for the best A/O resistance is not known at this time. Protection, however, is not great enough to allow extended use in LEO without application of an atomic oxygen resistant coating on the surface. Fluorination may provide better atomic oxygen resistance at coating defect sites.

Thermally Conductive Electrical Insulator

Electrically insulative graphite fluoride fiber has a high thermal conductivity value (at least five times higher than fiberglass). Therefore, it can be used as a heat sinking printed circuit board material for power electronics in spacecraft. Such an electronic system would have the advantage of lower electronics temperature, and therefore, higher efficiency and longer life.

Tailor-Made CTE and Electrical Resistivity

The characterization results described above suggest that, with proper control of the fluorination process, partially or fully fluorinated fibers with predetermined physical properties tailor-made to meet the requirements of certain engineering designs can be produced. For example, a partially fluorinated graphite fiber may have any CTE value between that of pristine graphite fiber (-1.5 ppm/°C) and fully fluorinated graphite fiber (more than 7 ppm/°C). It therefore would be suitable for use in solar concentrators in solar dynamic power system. In this case, a sharp focus of solar energy in a wide temperature range would be possible if the solar concentrator was made to have a near zero CTE value. Also, different layers of the solar concentrator, namely, the graphite epoxy composite layer and the metal coating on the composite layer

may become more CTE compatible, and therefore better adhered, if the graphite fibers used in the composite were replaced by the graphite fluoride fibers.

The graphite fluoride fibers could also have a predetermined electrical resistivity in the 10^4 to 10^{11} Ω-cm range and be suitable for use as a radar absorbing materials.

CONCLUSION

Graphite fluoride fibers can be an electrical insulator that conduct heat. By adjusting the fluorine content in the fiber, its physical properties can be tailor-made to meet the requirements of certain engineering designs. It may be less reactive to the LEO atomic oxygen than pristine graphite fiber. It is therefore potentially useful in many space applications. The physical properties obtained from previous characterization already indicate that this new material is useful. Further optimization of the graphite fluoride fabrication process should upgrade these physical properties even more. These physical properties are being used in connection with a detailed study of the heat sinking printed circuit board to determine the benefit of using the graphite fluoride fibers in this application. The printed circuit board application is selected among the applications described in this report because it seems to be the most promising application. Quantitative results of this analysis can then be used for the design and construction of the printed circuit board for power electronics in spacecraft.

REFERENCES

1. Ruff, O., and Bretschneider, O., "Neues Aus Der Chemie Des Fluors," Z. Anorg. U. Allgem. Chem., **217**, 1 (1934).

2. Watanabe, N., et al., "Process for Producing a Graphite Fluoride Comprising Mainly Polydicarbon Monofluoride Represented by the Formula $(C_2F)N$; Reaction of Graphite Material with Fluorine in the Presence of a Fluoride," U.S. Pat. 4,423,261 (Dec. 1983).

3. Watanabe, N., and Nakajima, T., "Graphite Fluoride," Preparation Properties and Industrial Applications of Organoflurine Compounds, R.E. Banks, ed., John Wiley and Sons, 297 (1982).

4. Hung, C., et al., "Synthesis, Electrical and Thermal Conductivities, and Potential Applications of Graphite Fluoride Fibers," SAMPE Q., **19**, 12 (1988).

5. Hung, C., and Long, M., "Fluorinated Graphite Fibers as a New Engineering Material: Promises and Challenges," NASA TM-102511 (1989).

6. Sinclair, D., "A Bending Method for Measurement of the Tensile Strength and Young's Modulus of Glass Fibers," J. Appl. Phys., **21**, 380 (1950).

7. Panna, F., Custom Compounding Inc., Aston, PA. Personal Communication.

8. Banks, B., and Rutledge, S., "Low Earth Orbital Atomic Oxygen Simulation for Materials Durability Evaluation," European Symposium on Spacecraft Materials in Space Environment, 4th, Toulouse, France, Sept. 6-9, 1988, *Proceedings*, Cepadues Editions, Toulouse, France, 371, (1989).

9. Rutledge, S., NASA Lewis Research Center, Cleveland, OH, Personal Communication.

TABLE I. - EFFECT OF SIMULATED ATOMIC OXYGEN ENVIRONMENT ON DIFFERENT KINDS OF FIBERS

[The 0.1 eV simulated atomic oxygen had Kapton equivalent fluence of 1.44×10^{20} atom/cm^2. The weight data were from exposing strands of fibers in an open vial. The diameter and electrical resistance data from exposing individual fibers on glass slide.]

	Halogen to carbon weight ratio, percent		Weight loss, percent	Diameter increase,[a] percent		Resistance increase,[b] percent	
	F	Br		A[c]	B[c]	A[c]	B[c]
P-100[d]	0	0	3.88	4.1	[e]17	62	44
P-100	3.7	0	1.91	4.8	-2.1	-5	4
P-100	97	Trace	3.62	-4.6	-3.6	(f)	(f)
P-100	12	14	6.53	-------	-----	---	---
P-100	0	18	6.93	-------	-----	---	---
P-55[d]	0	0	5.09	[e]5.5	6.7	46	46
P-55	<1	0	4.24	6.3	0	23	21
P-25[d]	0	0	5.48	[g]-100	0	∞	21
P-25	.6	0	4.58	-18	-7.8	56	40
S-fiberglass	0	0	1.16	0	1	(f)	(f)

[a]After simulated atomic oxygen exposure, only fiberglass has uniform diameter along the length of the fiber. Therefore average values of three measurements at three different points are used.

[b]Contact resistance between the fibers and the sample holder is not stable in the first 20 min of the simulated atomic oxygen exposure. Therefore, the resistance change described in this table is the change from 20 min exposure to 20 hr exposure.

[c]A and B are the two fibers to be examined.

[d]The graphite interplanar spacings for P-100, P-55 and P-25 are 3.37, 3.42, and 3.45 Å, respectively. The closer the interplanar spacing to 3.35 Å, the more graphitized the graphite fibers are.

[e]Damages of these fibers are visible under the x780 optical microscope.

[f]The resistance of these fibers is too high to be measured.

[g]This fiber disappeared completely, probably totally oxidized by the atomic oxygen.

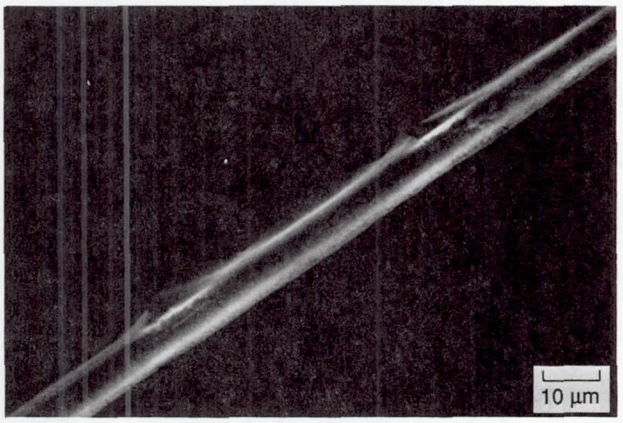

Figure 1.—Micrograph of the P-55 graphite fiber after it was exposed to the 0.1 eV simulated atomic oxygen at $2x10^{15}$ atm/cm^2-sec Kapton equivalent flux for 20 hours.

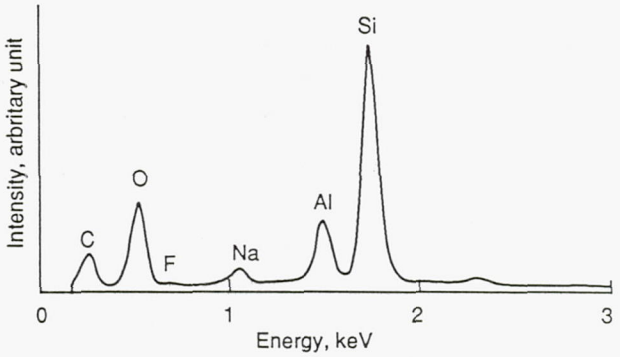

Figure 2.—Energy disperse spectrum of the P-100 graphite fiber after it was exposed to the 0.1 eV simulated atomic oxygen at $2x10^{15}$ atm/cm^2-sec Kapton equivalent flux for 20 hours.

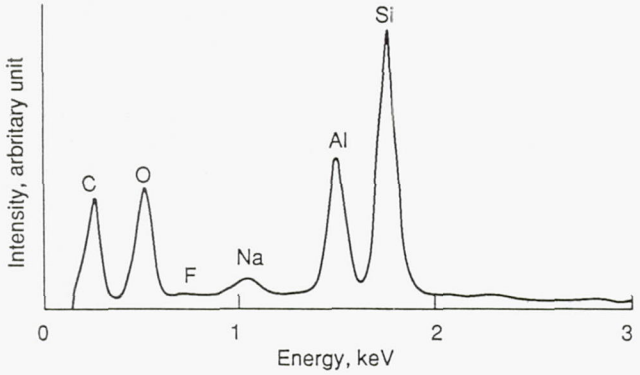

Figure 3.—Energy disperse spectrum of the P-100 graphite fiber after it was fluorinated to gain 3.7 percent weight and then exposed to the 0.1 eV simulated atomic oxygen at $2x10^{15}$ atm/cm^2-sec Kapton equivalent flux for 20 hours.

NASA
National Aeronautics and Space Administration

Report Documentation Page

1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.
NASA TM-103265		

4. Title and Subtitle	5. Report Date
Graphite Fluoride Fibers and Their Applications in the Space Industry	6. Performing Organization Code

7. Author(s)	8. Performing Organization Report No.
Ching-chen Hung, Martin Long, and Therese Dever	E-5679
	10. Work Unit No. 505-41-41

9. Performing Organization Name and Address	11. Contract or Grant No.
National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135-3191	13. Type of Report and Period Covered Technical Memorandum

12. Sponsoring Agency Name and Address	14. Sponsoring Agency Code
National Aeronautics and Space Administration Washington, D.C. 20546-0001	

15. Supplementary Notes

Prepared for the 1990 AIChE Summer National Meeting, San Diego, California, August 19-22, 1990. Ching-chen Hung, NASA Lewis Research Center. Martin Long and Therese Dever, Cleveland State University, Cleveland, Ohio 44115.

16. Abstract

Characterization and potential space applications of graphite fluoride fibers from commercially available graphitized carbon fibers are presented in this report. Graphite fluoride fibers with fluorine-to-carbon ratios of 0.65 and 0.68 were found to have electrical resistivity values of 10^4 Ω-cm and 10^{11} Ω-cm, respectively, and thermal conductivity values of 24 and 5 W/m-K, respectively. At this fluorine content range, the fibers have tensile strength of 0.25 ± 0.10 GPa (36 ± 14 ksi), Young's modulus of 170 ± 30 GPa (25 ± 5 Msi). The CTE value of a sample with fluorine-to-carbon atom ratio of 0.61 was found to be 7 ppm/°C. These properties change and approach the graphite value as the fluorine content approaches zero. Electrically insulative graphite fluoride fiber is at least five times more thermally conductive than fiberglass. Therefore, it can be used as a heat sinking printed circuit board material for low temperature, long life power electronics in spacecraft. Also, partially fluorinated fibers with tailor-made physical properties to meet the requirements of certain engineering design can be produced. For example, a partially fluorinated fiber could have a predetermined CTE value in -1.5 to 7 ppm/°C range and would be suitable for use in solar concentrators in solar dynamic power systems. It could also have a predetermined electrical resistivity value suitable for use as a low observable material. Experimental data indicate that slightly fluorinated graphite fibers are more durable in the atomic oxygen environment than pristine graphite. Therefore, fluorination of graphite used in the construction of spacecraft that would be exposed to the low Earth orbit atomic oxygen may protect defect sites in atomic oxygen protective coatings and therefore decrease the rate of degradation of graphite.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Fluorinated carbon fibers Atomic oxygen Tailor-made properties	Unclassified - Unlimited Subject Category 23

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of pages	22. Price*
Unclassified	Unclassified	10	A

*For sale by the National Technical Information Service, Springfield, Virginia 22161